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The Effects of Process Parameters on Injection-Molded PZT Ceramics Part Fabrication- Compounding Process Rheology

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Abstract

Solid solutions of lead-based perovskites are the backbone materials of the piezoelectric components for transducer, actuator, and resonator applications. These components, typically small in size, are fabricated from large sintered ceramic slugs using grinding and lapping processes. These operations increase manufacturing costs and produce a large hazardous waste stream, especially when component size decreases. To reduce costs and hazardous wastes associated with the production of these components, an injection molding technique is being investigated to replace the machining processes. The first step in the new technique is to compound an organic carrier with a ceramic powder. The organic carrier is a thermoplastic-based system composed of a main carrier, a binder, and a surfactant. Understanding the rheology of the compounded material is necessary to minimize the creation of defects such as voids or cavities during the injection-molding process. An experiment was performed to model the effects of changes in the composition and processing of the material on the rheological behavior. Factors studied included: the surfactant of the organic carrier system, the solid loading of the compounded material, and compounding time. The effects of these factors on the viscosity of the material were investigated.

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Executive Summary

Solid solutions of lead-based perovskites are the backbone materials of the piezoelectric components for transducer, actuator, and resonator applications. These components, typically small in size, are fabricated from large sintered ceramic slugs using grinding and lapping processes. These operations increase manufacturing costs and produce a large hazardous waste stream, especially when component size decreases. To reduce costs and hazardous wastes associated with the production of these components, an injection molding technique is being investigated to replace the machining processes. The first step in the new technique is to compound an organic carrier with a ceramic powder. The organic carrier is a thermoplastic-based system composed of a main carrier, a binder, and a surfactant. Understanding the rheology of the compounded material is necessary to minimize the creation of defects such as voids or cavities during the injection-molding process. An experiment was performed to model the effects of changes in the composition and processing of the material on the rheological behavior. Factors studied included: the surfactant of the organic carrier system, the solid loading of the compounded material, and compounding time. The effects of these factors on the viscosity of the material were investigated. The results of the experiment are as follows.

1. Increasing solid loading increased the viscosity of the PZT material. In addition, it increased the variation in the viscosity of the material.
2. Increasing surfactant decreased the viscosity of the PZT material and its variation.
3. At high solid loading, increased mixing time decreased the viscosity of the PZT material. Increasing mixing time also reduced the variation in viscosity of the material regardless of the amount of solid loading.

Since the goal of the experiment was to minimize the viscosity of the material and its variation, optimum compounding process conditions would be to minimize solid loading, maximize the surfactant, and mix the material for at least 50 minutes. However, because of tight dimensional requirements on the parts after injection-molding, it is desirable to maximize solid loading. Thus, the conditions determined to be optimum for the compounding process are high solid loading, high surfactant, and 50 minutes minimum mixing time.

I. Introduction

This report documents the results of an experiment performed to characterize the effects of compounding process parameters on the rheology of injection-molded Lead Zirconate Titanate (PZT) ceramics. PZT ceramics are used by Sandia in shock-wave induced power supply applications. The current process for fabricating these parts involves forming the ceramic, sintering, machining, and assembly. The machining processes have several disadvantages. First, these processes tend to introduce defects (chips and cracks) into the parts. Second, these processes are labor intensive. Third, because the parts are very small and a lead-deficient surface layer resulting from high-temperature sintering needs to be removed, the machining processes tend to remove as much material as remains in the machined part. Thus, the amount of waste created in the processes is at least 40% of the original material. Since this material contains lead, it is classified as hazardous waste. Therefore, the machining processes include required special environmental and safety procedures to contain and dispose of the waste. Injection-molding is a near net-shape forming process that would potentially eliminate machining processes in the fabrication of the parts. The new process would consist of compounding the material, injection-molding the parts, sintering, and assembly.

This report will discuss the rheological characterization of the compounding process. SAND2005-TBD¹ will discuss the characterization of the effects of injection-molding parameters on the density and dimensions of molded parts.

The rheology of the compounded material is critical to the performance of the injection-molding process. Minimizing the viscosity of the material is beneficial for die-filling and therefore is expected to reduce defects and warping. In addition, material with a consistent viscosity will produce injection-molded parts with more consistent densities and dimensions. Thus, the goal of the compounding process characterization is to minimize the viscosity of the compounded material and its variability.

A statistically designed experiment was used to characterize the compounding process. These designs are intended to maximize the information to be gained in an experiment while minimizing the number of tests required. In addition, the statistical analysis of the experimental data assures that the conclusions drawn from the experiment are valid and objective. Factors controlled during the experiment were the solid loading percentage, the surfactant percentage, and mixing time. The effects of these factors on the rheology of the compounding material were investigated.

II. Injection Molding Process

The current and proposed processes for fabricating ceramic parts are given in Figure 1. Figure 2 provides an example of the type of defects induced by processes such as lapping, grinding, and slicing. The proposed injection-molding process consists of:

- A compounding process, and
- An injection-molding process.

This report documents the result of an experiment used to characterize the compounding process. SAND2005-TBD gives the results of the characterization of the injection-molding process.

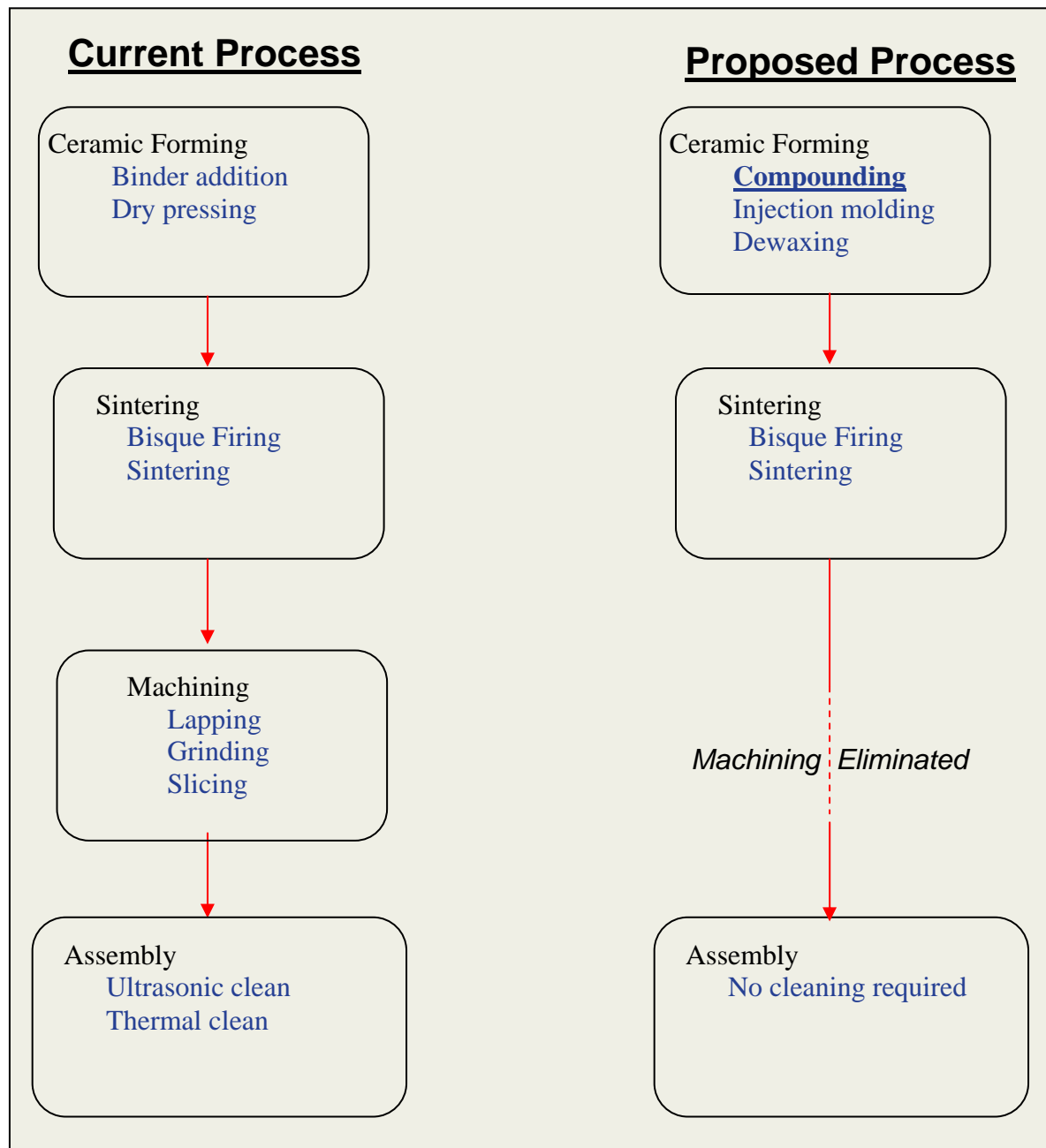


Figure 1. Current vs. Proposed Ceramic Part Fabrication Process

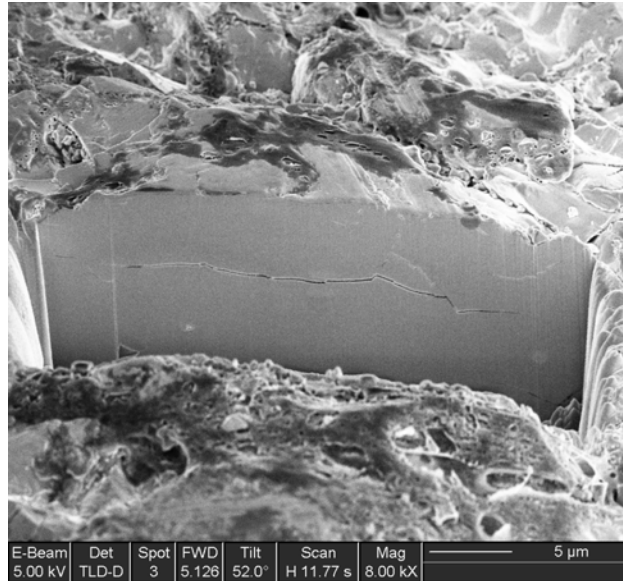


Figure 2. Crack in Fabricated Ceramic Part Induced by Machining

III. Experimental Design

To characterize the compounding process, we used a structured experimental design process. The steps in this process are:

- Define the objective of the experiment;
- Identify the response variables or outputs of the process to be investigated;
- Identify the factors or inputs of the process to be investigated;
- Identify factor levels to be controlled in the experiment and the experimental design to be used; and
- Conduct the experiment, and analyze and confirm the results.

Objectives And Response Variables

The objective of the experiment was to determine what factor combinations would minimize the viscosity of the PZT material and its variability while maximizing solid loading. Solid loading refers to the amount of PZT ceramic in the compounded material. It is desirable to maximize solid loading so that there is less shrinkage in the parts during subsequent dewaxing and sintering processes. Shrinkage is undesirable since it increases the unpredictability in the dimensions of the fabricated parts. However, one of the factors that limits the maximization of solid loading is the particle size of the PZT material. Smaller particle sizes increase the total surface area of the PZT ceramic which in turn requires more organic in the carrier system to provide an appropriate viscosity for the injection molding process. If the material is too viscous it cannot produce consistent feedstock and will not be injection-molded. The mean diameter for the PZT ceramic used in this experiment is approximately one micron. Given this particle size, the maximum solid loading is limited to 47.5 volume %.

The response variables chosen to measure these objectives were:

- Viscosity measured in Pa-s over a varying shear rate, and
- The natural log of the standard deviation of the viscosity over a constant shear rate of approximately 3000/sec. This selected shear rate is determined by the gate design of the mold. The natural log is chosen in order to homogenize the variance and meet the normality assumption of the Analysis of Variance technique (ANOVA) used to analyze the data. The distribution of standard deviations tends to be non-normal. Values are only positive and the distribution is often skewed to the right. The natural log transformation “normalizes” the response to meet the assumption of the ANOVA technique.

These measurements were made by a capillary rheometer (see Figure 3). The temperature of the material as it passed through the rheometer was held constant at 120°C. The typical processing window for injection-molding is approximately 20°C above solidification temperature of the organic carrier system. Solidification temperature for the system is approximately 94°C. The diameter of the capillary was 30 mils. The plunger speed was used to vary and hold constant the shear rate for the viscosity measurements. The stress was determined by the pressure transducer near the capillary.

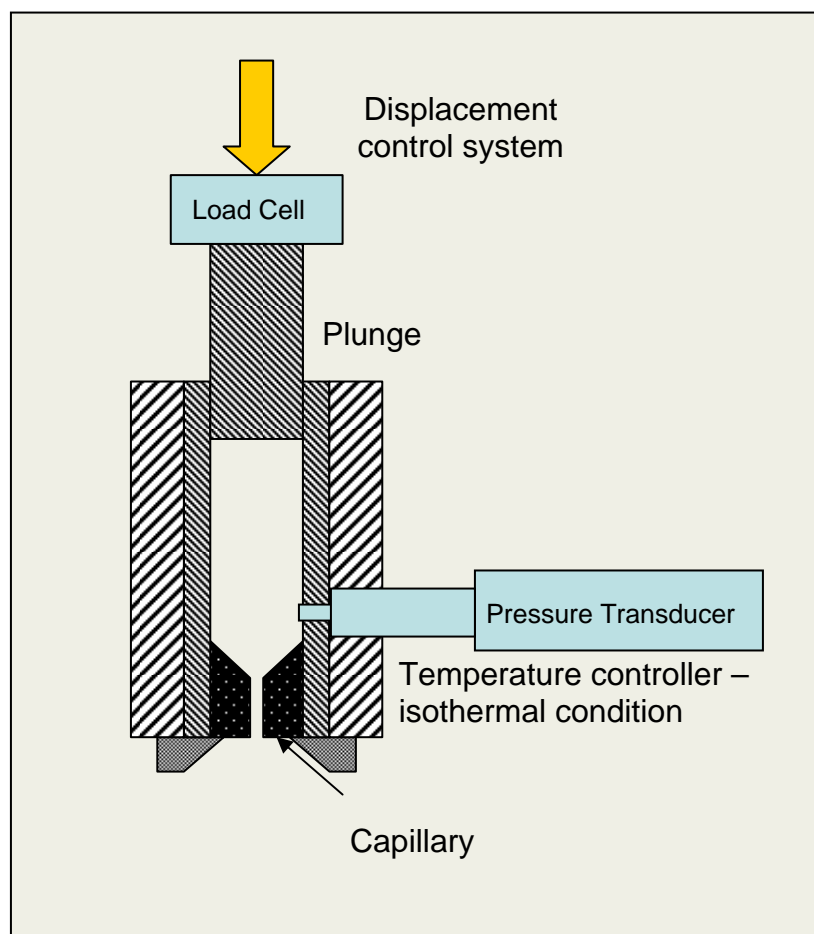


Figure 3. Capillary Rheometer

Identify Factors To Be Investigated In The Experiment

The baseline compounding process consists of the following input materials:

- A binder system, a thermoplastic-based system which included
 - paraffin wax, a straight-chain hydrocarbon wax derived from petroleum refining process,
 - proFlow 3000, and polypropylene and polyethylene random copolymer, and
 - stearic acid, surfactant ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$); and
- PZT ceramic particles with a mean diameter of approximately one micron (see Figure 4).

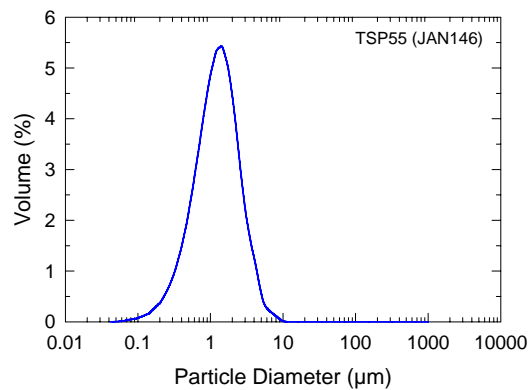


Figure 4. Distribution of PZT Particle Size

Table 1 gives the baseline proportions for these materials that make up the PZT compound.

Material	Density (g/cm3)	Volume %	Weight %
Paraffin wax	0.90 ~ 0.93	28.75	50
proFlow 3000	0.92	25.54	45
Stearic acid	0.84	2.71	5
PZT Ceramic	7.97	45	-

Table 1. Baseline PZT Material Proportions

These materials were pre-mixed at 150°C at 60 rpm for 15 minutes in a C. W. Brabender, a three-piece mixer with twin roller blades. Pre-mixing continued until the temperature ramped down to approximately 110°C and peak torque was reached. It was at this point that agglomerations in the material began to break apart and the material became more consistent. The material was then mixed for another fixed amount of time to assure complete blending. This subsequent mixing time was measured from peak torque (see Figure 5).

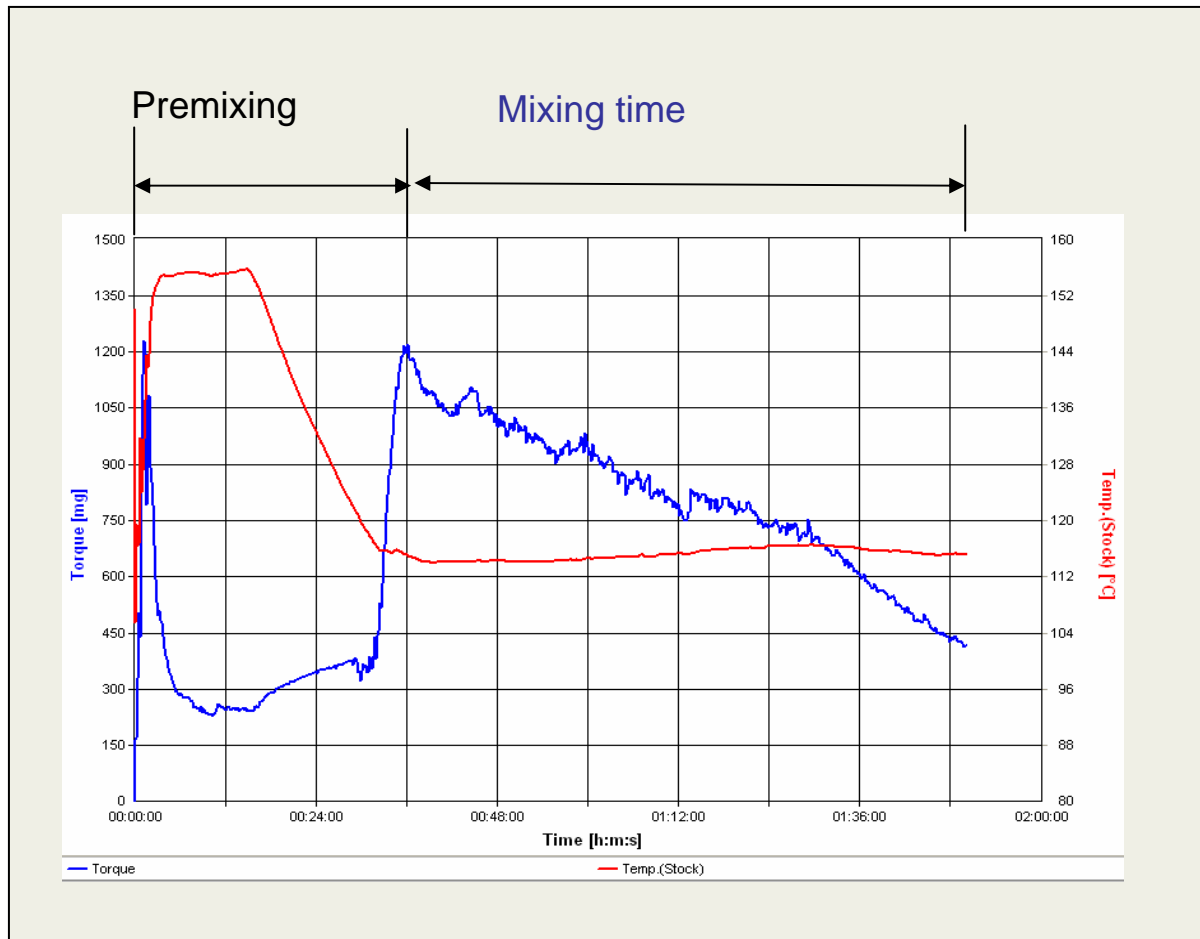


Figure 5. Torque and Temperature Profile for Compound Mixing Process

Identify Factor Levels To Be Controlled In The Experiment And The Experimental Design To Be Used

We decided to investigate the effects of the following factors on the viscosity of the mixed material:

- Surfactant at 2, 3.5 and 5%;
- Solid loading at 40, 42.5, 45, and 47.5%; and
- Mixing Time at 10, 30, 50, and 70 minutes.

The design chosen to study these effects was a 3x4x4 general full factorial design. This design allows for all unique combinations of factor levels to be run. Figure 5 provides a graphical representation of the runs performed in the experiment. The order in which the runs were performed is given in Table 2. Each batch was processed for the allotted mixing time and viscosity measurements were then taken. This process was repeated for all mixing times.

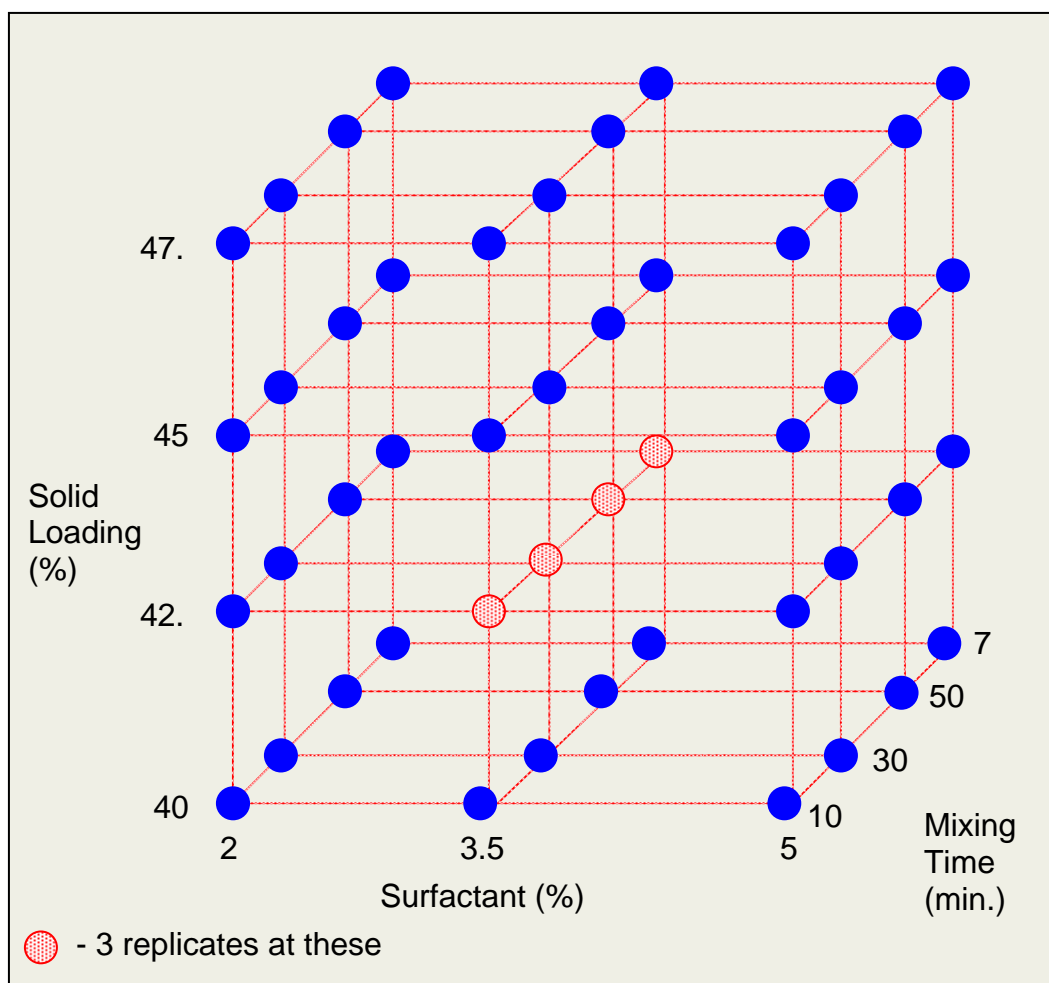


Figure 5. Graphical Representation of Runs Performed in the Experiment

Batch Number	Solid Loading (%)	Surfactant (%)	Mixing Time (minutes)
5a	42.5	3.5	10, 30, 50, 70
2	40	3.5	10, 30, 50, 70
1	40	2	10, 30, 50, 70
4	42.5	2	10, 30, 50, 70
5b	42.5	3.5	10, 30, 50, 70
6	42.5	5	10, 30, 50, 70
9	45	5	10, 30, 50, 70
7	45	2	10, 30, 50, 70
3	40	5	10, 30, 50, 70
5c	42.5	3.5	10, 30, 50, 70
12	47.5	5	10, 30, 50, 70
13	47.5	3.5	10, 30, 50, 70
8	45	3.5	10, 30, 50, 70

Table 2. Experimental Design Run Order

IV. Analysis of Experimental Data

Plot And Look

Analysis began by plotting and looking at the data to determine if there were any anomalies that needed to be removed before proceeding with the statistical analysis. Figure 6 displays a set of scatter plots of the $\log_{10}(\text{viscosity})$ vs. $\log_{10}(\text{shear rate})$. The red arrow points to an anomaly in the original data set. The first batch of material to be processed by the mixer, 5a, at its lowest mixing time of 10 minutes behaved very differently from the other two batches (5b and 5c) mixed for 10 minutes and composed of the same amounts of surfactant and solid loading. It was determined that this run was an anomaly because a new technologist inexperienced with the equipment was needed to mix the first batch and was inadequately trained in the process. Therefore, these data were removed from subsequent analyses. The figure also shows that there are some “kinks” in the viscosity/apparent shear rate relationships. No explanation for this behavior was found. However, these “discontinuities” occurred at low apparent shear rates ($\approx 100/\text{second}$). Since we are only interested in the viscosity of the material between shear rates of 1000-3000/second, the operational range for the gate design, we ignored this phenomenon. Finally, data for solid loading at 47.5 and surfactant at 2% was lost. The material was too viscous to obtain measurements from the rheometer.

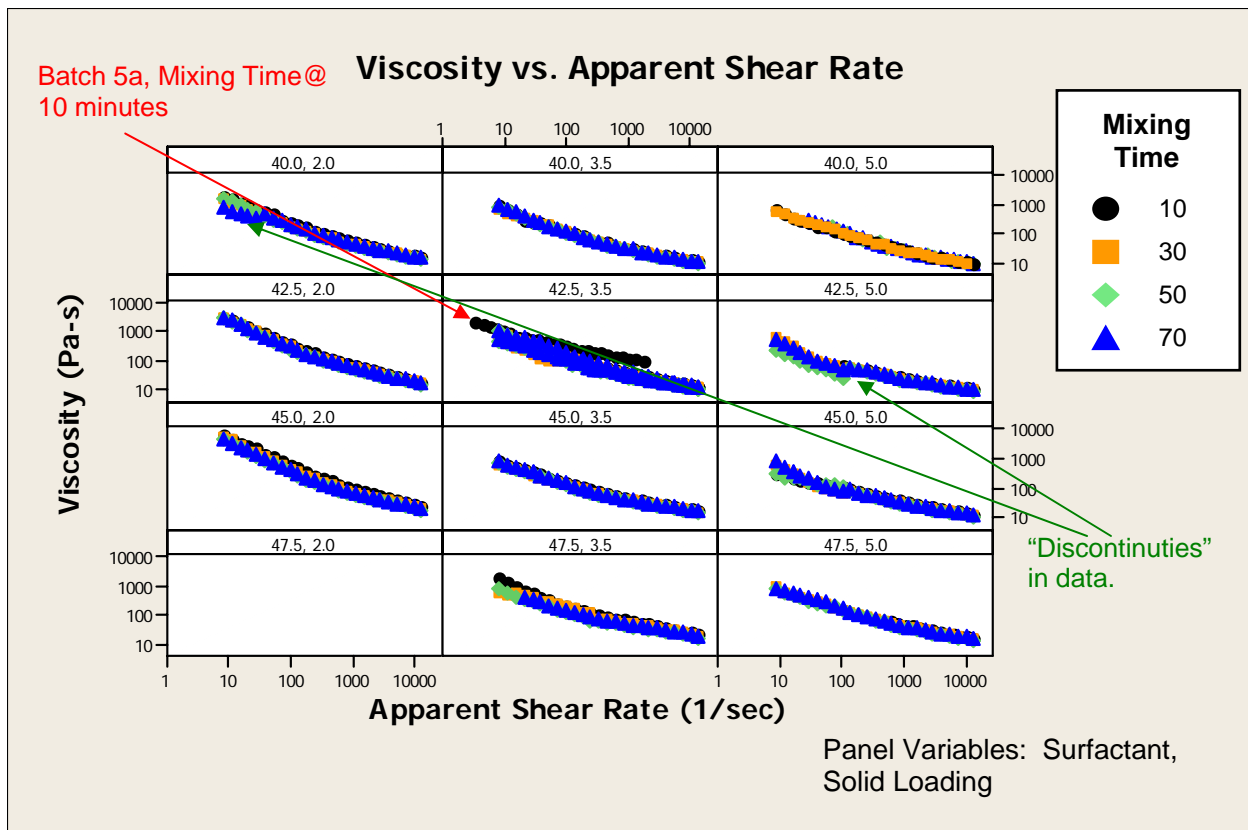


Figure 6. Viscosity versus Apparent Shear Rate (log-log scale)

Rabinowitsch Correction Of Viscosity And Shear Rate

The rheology of the injection-molded material exhibits shear thinning behavior. Therefore, the shear rate and viscosity values must be adjusted with the Rabinowitsch correction.² This correction consisted of four steps.

1. We performed a least-squares fit of the natural log of the material stress (σ_w) with respect to the natural log of the shear rate (γ) for shear rate values greater than or equal to 1000/sec. We limited the analysis to these values because the power law does not fit the data well for shear rates of 1000/sec or less. In addition, we were only interested in shear rates between 1000 and 3000/sec as an operating window for injection molding. This fitted equation was:

$$\ln(\sigma_w) = 17.73 + 0.63 * \ln(\gamma) + \text{other terms} + \varepsilon$$

2. We calculated the first derivative of $\ln(\sigma_w)$ with respect to $\ln(\gamma)$. This derivative is denoted n' . From the equation above we got:

$$n' = \frac{d(\ln(\sigma_w))}{d(\ln(\gamma))} = 0.63$$

3. We calculated the corrected shear rate.

$$\gamma_w = \frac{3n' + 1}{4n'} \gamma = 1.15\gamma$$

4. We calculated the viscosity based on the corrected shear rate.

$$\eta = \frac{\sigma_w}{\gamma_w}$$

These corrected values were then used in the analysis of the experimental data. We analyzed both response variables:

- Viscosity measured in Pa-s over a varying shear rate, and
- The natural log of the standard deviation of the viscosity over a constant shear rate of approximately 3000/sec.

Analysis Of Viscosity At Varying Shear Rates

A plot of the viscosity data versus shear rate shows that the data, as expected, follows the power law relationship (see Figure 7).

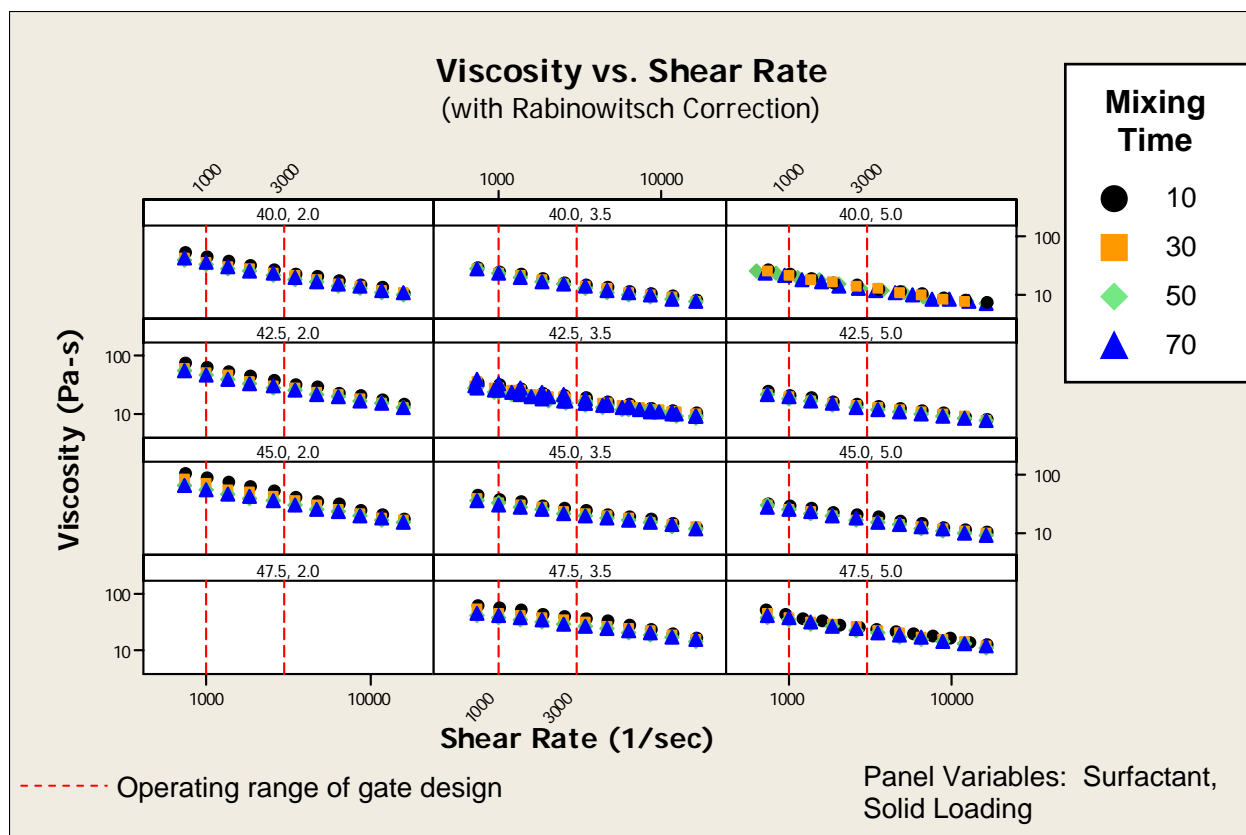


Figure 7. Viscosity by Shear Rate with Rabinowitsch Correction (log-log scale)

Since we were interested in viscosities between shear rates of 1000 to 3000/sec, we removed data outside that range for subsequent analysis.

Next, we created interaction plots of the experimental data. Interaction plots are plots of the average response (in this case, viscosity) for each level of a factor with the level of a second factor held constant. All other levels of factor levels are included in the averaging. For example, we see from Figure 8 that the average viscosity is estimated to be 47.31 for surfactant at 2% and solid loading at 45%. This value was obtained by averaging all data collected within 1000-3000/sec and over all mixing times of 10, 30, 50, and 70 minutes. Table 3 gives all the data collected for surfactant at a level of 2% and solid loading at a level of 45%. In addition, the average viscosity for these data is given. Thus, each data point on interaction plots represent a unique combination of two factors at a time.

These plots are useful for judging the magnitude of single-factor and two-factor terms in models. Low levels of surfactant appear to significantly increase viscosity. The panel in Figure 8 that depicts the average viscosity for various combinations of levels of solid loading and mixing times can be misleading. Since the viscosity averages for the highest solid loading level (47.5%) did not include 2% surfactant data, these values may be artificially low. Figure 9 gives interaction plots of the experimental data with surfactant at 2% removed. The average viscosities for solid loading at 45% have dropped considerably. The average difference between viscosities for the 45% solid loading material with the 2% surfactant data and without it is 9 Pa-s. Thus, both figures must be used to properly interpret the results of the experiment.

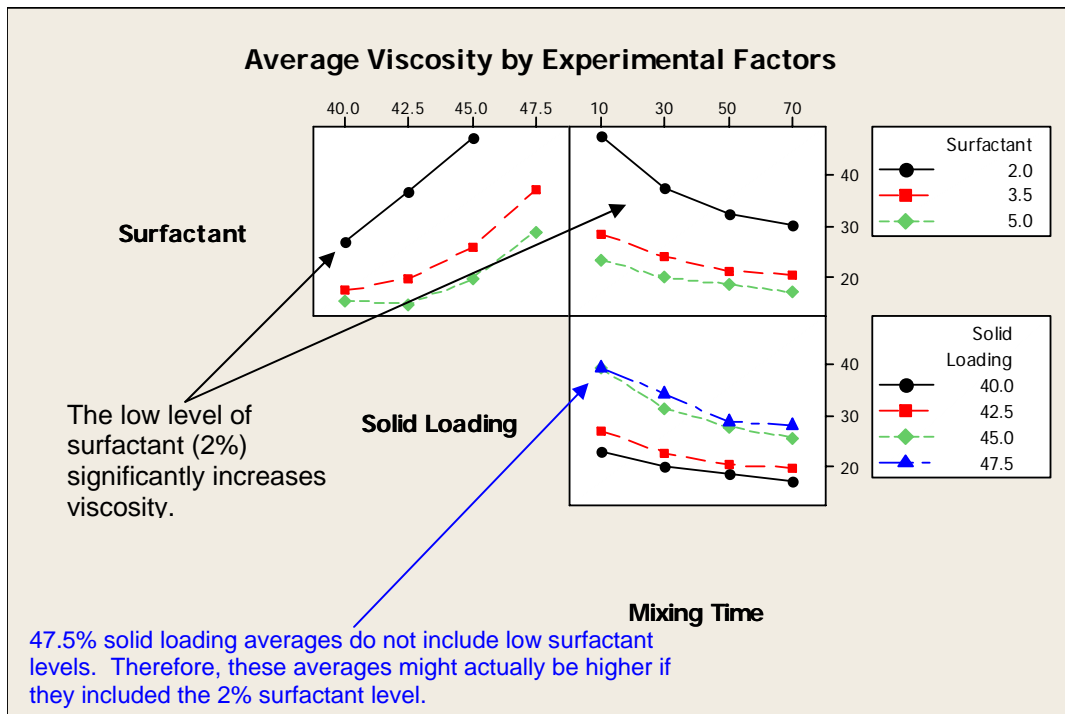


Figure 8. Interaction Plot of Viscosity vs. Surfactant, Solid Loading, & Mixing Time

Batch Number	Solid Loading (Vol %)	Surfactant (Wt %)	Mixing Time (Min)	Shear Rate (1/sec)	Viscosity (Pa-s)
7	45	2	10	1360.5	74.985
7	45	2	10	1853.4	62.983
7	45	2	10	2524.5	52.873
7	45	2	30	1360.5	56.078
7	45	2	30	1853.4	48.448
7	45	2	30	2524.5	40.384
7	45	2	50	1360.5	46.698
7	45	2	50	1853.4	40.07
7	45	2	50	2524.5	34.259
7	45	2	70	1360.5	43.026
7	45	2	70	1853.4	36.864
7	45	2	70	2524.5	31.05
Average Viscosity					47.31

Table 3. Example of Calculation of Interaction Plot Data Points

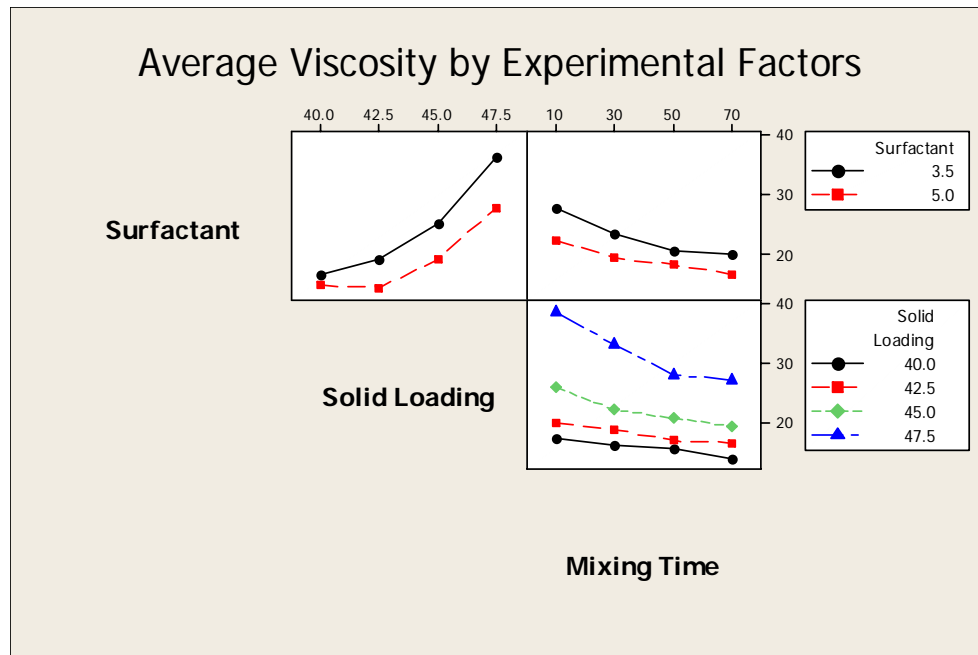


Figure 9. Interaction Plot of Viscosity vs. Surfactant, Solid Loading and Mixing Time without Low Surfactant

From Figures 8 and 9 we can conclude the following.

- Increasing surfactant decreases viscosity. This effect is larger for higher values of solid loading and for shorter mixing times and indicates that there are interactions between these factors. In addition, the effect appears to be nonlinear.
- Decreasing solid loading decreases viscosity. The effect appears to be nonlinear.
- Increasing mixing time decreases viscosity. The effect is more pronounced for higher levels of solid loading and indicates that there is an interaction between this factor and mixing time. Increasing the time from 50 to 70 minutes has little effect on viscosity.
- Solid loading and surfactant have the most significant effect on viscosity. Depending on the level of surfactant, the effect of increasing solid loading from 40 to 47.5% is an increase in viscosity of 14-20 Pa-s. Depending on the level of solid loading, the effect of increasing surfactant from 2 to 5% is a decrease in viscosity of 12-27 Pa-s. Increasing mixing time from 10 to 70 minutes for low levels of surfactant or high levels of solid loading decreases viscosity on average by 17.5 and 11.5 Pa-s, respectively.
- Increasing surfactant and mixing time mitigates to some extent increases in viscosity due to increases in solid loading.

Analysis of Variance (ANOVA) was used to statistically analyze the data.³ Assumptions made by this method must be tested for the analysis to be valid. These assumptions are that the experimental error, ϵ , also referred to as residuals should be random and normally distributed with a constant variance across the design space. These assumptions are assessed graphically in Figure 10. The two graphs on the left of the figure are used to assess the normality assumption. The graph on the upper right is used to assess the randomness and constant variance assumption. Finally, the lower right graph is used to assess order randomness. The Normal Probability Plot in the upper left corner of the figure shows three red points that do not lie along the normal probability line. Data distant from the line indicates non-normality in the residuals. The

deviation is small but it does warrant further investigation. The normality assumption of the ANOVA method is robust to some non-normality. However, looking at the graph on the lower right of the figure, it is apparent that these three values are not randomly spread across the run order of the data but are from the same batch, 5b, and all have the same mixing time of 70 minutes. This might lead one to conclude that there may have been some deviation in processing that caused these samples to exhibit higher viscosities than expected.

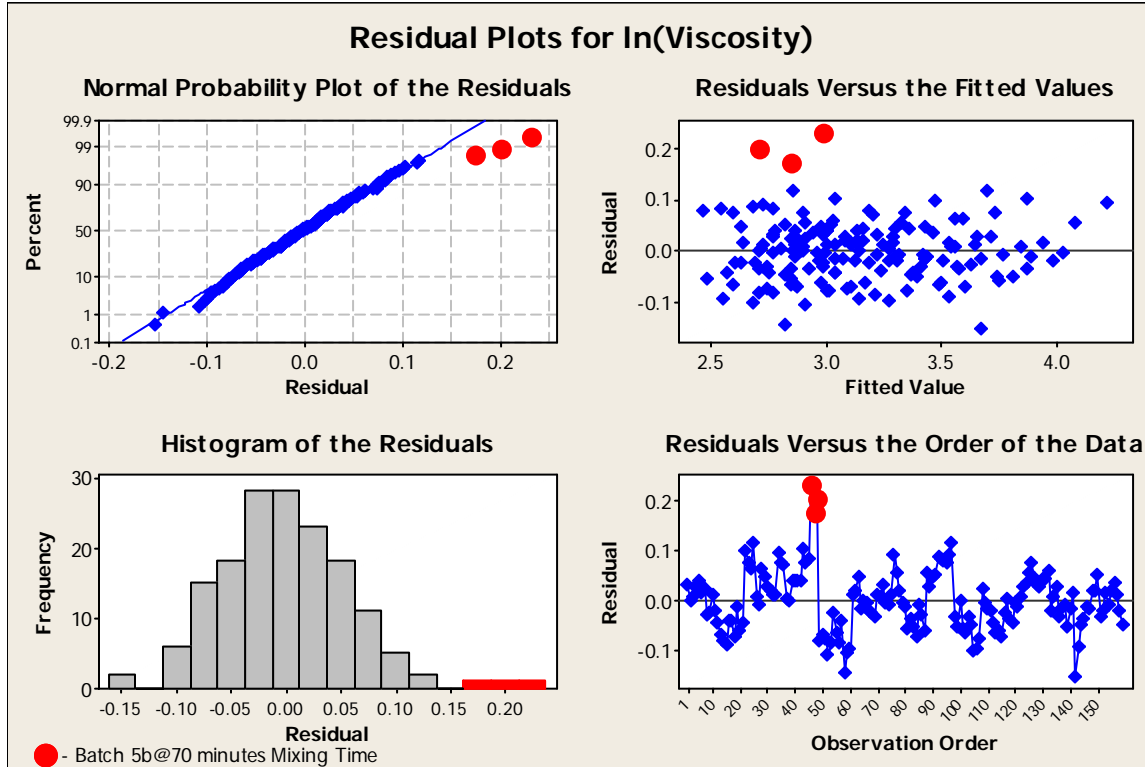


Figure 10. ANOVA Tests for Residuals

However, the deviations were small and removing these points from the analysis did not significantly alter the final fitted model. The final model including these unusual observations was:

$$\begin{aligned} \ln(\eta) = & 20.29 - 70.55 * \text{Solid Loading} - 14.54 * \text{Surfactant} + 0.004 * \text{Mixing Time} - 0.44 * \ln(\gamma_w) \\ & + 100.76 * \text{Solid Loading}^2 + 731.75 * \text{Surfactant}^2 + 0.0001 * \text{Mixing Time}^2 \\ & - 156.38 * \text{Solid Loading} * \text{Surfactant} - 0.039 * \text{Solid Loading} * \text{Mixing Time} \\ & + 0.113 * \text{Surfactant} * \text{Mixing Time} \end{aligned}$$

The units for each of the factors in the model are:

- solid loading in fraction volume,
- surfactant in fraction weight, and
- mixing time in minutes.

The adjusted R^2 for this model was 97.4%. This statistic provides a measure of percentage of the variability in the data that is explained by the model. An R^2 of 97% is considered a very good fit.

The levels of the factors that minimize the viscosity based on this model are:

- Solid Loading at 40%,
- Surfactant at 5%, and
- Mixing Time at 70 minutes.

These values according to this model will yield material with an approximate viscosity of 11.64 Pa-s.

However, another objective was to maximize solid loading. If we maximize solid loading at 47.5%, with the surfactant at 5% and mixing time at 70 minutes, the model estimates the viscosity of the material to be approximately 20.54 Pa-s, nearly double the viscosity at low solid loading levels.

Analysis Of The Standard Deviation Of The Viscosity At A Constant Shear Rate

The data for this analysis consisted of taking several measurements of material flowing through the rheometer at a constant shear rate. Approximately 100 measurements were made for each batch. First, we plotted the data to identify any unusually variable conditions. Figure 11 depicts an individual value plot for the data. Outliers are circled. These values appear to be very different from other viscosity values for the same batch and mixing times (see Table 4). These data were removed from the analysis. Note that data from Batch 5b at 70 minutes were among the outliers. This batch and mixing time also exhibited unusual viscosity measures in the previous analysis (see Figure 10).

Batch Number	Solid Loading (%)	Surfactant (%)	Mixing Time (Minutes)	Number of Values Removed from Analysis
3	40	5	50	3
5b	42.5	3.5	70	13
5c	42.5	3.5	30	1

Table 4. Outliers in Constant Shear Rate Data

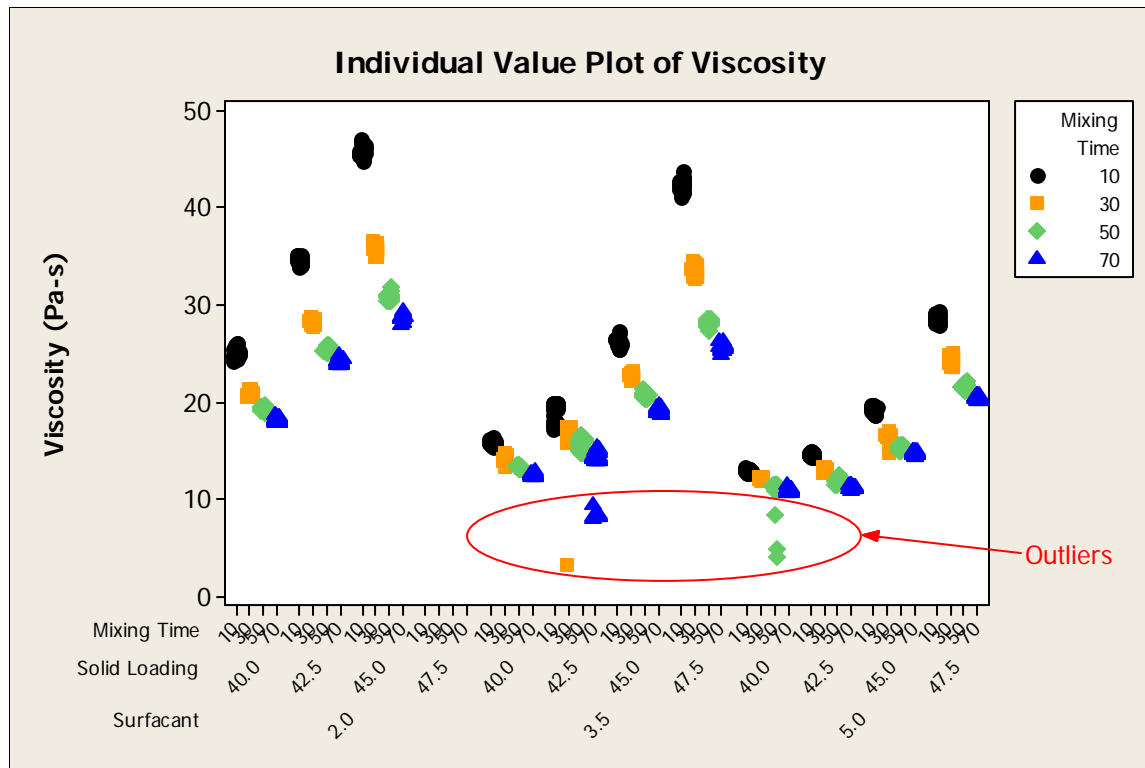


Figure 11. Individual Value Plot for Viscosity

Analysis of the standard deviation of the viscosity was performed on the natural log of the standard deviation, $\ln(\sigma_\eta)$. Figure 12 is a plot of the averages of these values at the levels of each experimental factor.

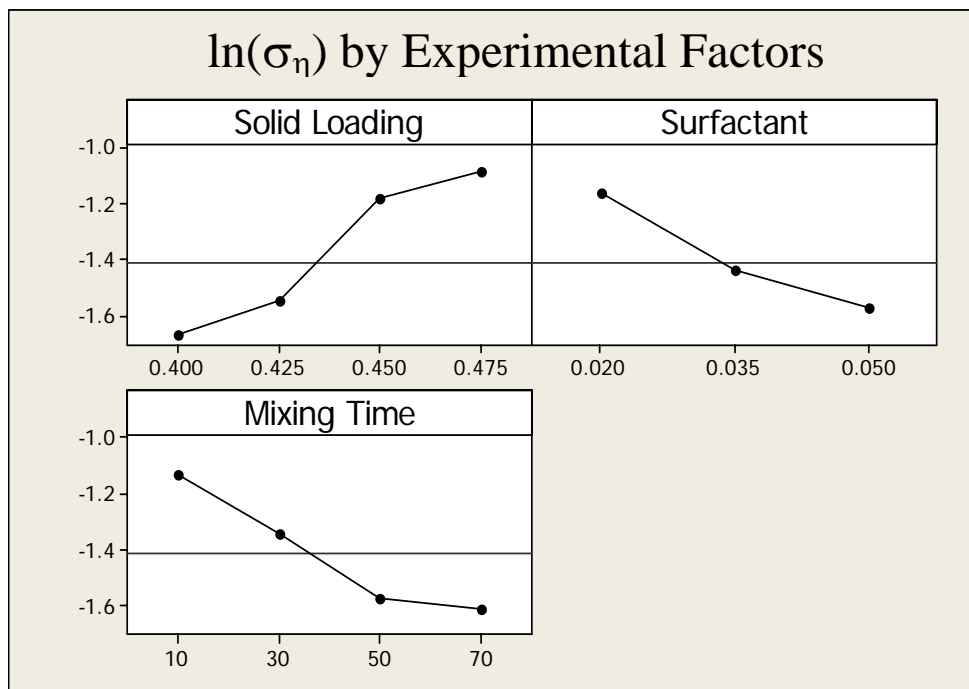


Figure 12. Plot of $\ln(\sigma_\eta)$ by Experimental Factors

The following conclusions can be drawn from this figure.

- The $\ln(\sigma_\eta)$ increases as solid loading increases.
- The $\ln(\sigma_\eta)$ decreases as surfactant & mixing time increases.
- There is a linear-to-threshold effect for mixing time.
- Increasing mixing time from 50 to 70 minutes has little effect on reducing $\ln(\sigma_\eta)$.

Statistical analysis of the data yielded the following model.

$$\ln(\sigma_\eta) = -5.05 + 10.75 * \text{Solid Loading} \\ - 18.81 * \text{Surfactant} \\ - 0.01 * \text{Mixing Time}$$

The adjusted R^2 for this model was 67.3%. This statistic is often lower for $\ln(\sigma)$ data but this value indicates that the model fits reasonably well.

The levels of the factors that minimize $\ln(\sigma_\eta)$ using the fitted model are:

- solid loading at 40%,
- surfactant at 5%, and
- mixing time at 70 minutes.

These values according to this model will yield material with an approximate σ_η of 0.10 Pa-s.

However, another objective was to maximize solid loading. If we maximize solid loading at 47.5%, with the surfactant at 5% and mixing time at 70 minutes, the model estimates the σ_η of the material to be approximately 0.22 Pa-s, double the σ_η at low solid loading levels. The estimated 99% confidence intervals for the viscosity at these levels are:

$$99\% \text{ CIs} = 20.54 \pm 3 * .22 = 20.54 \pm .66 = (19.88, 21.2 \text{ Pa-s})$$

V. Conclusions And Future Investigations

Conclusions to be drawn from the experiment are as follows. The best conditions for minimizing viscosity and its variation are:

- solid loading at 40%
- surfactant at 5%, and
- mixing time at 50 minutes minimum (little improvement is to be gained from increasing the mixing time to 70 minutes).

However, to meet dimensional part requirements, it is desirable to maximize the solid loading. Therefore, the best conditions for minimizing viscosity and its variation while maximizing solid loading are:

- Surfactant at 5%, and
- Mixing Time at 50 minutes minimum.

However, subsequent dewaxing of parts consisting of 5% surfactant has exhibited “slumping” (see Figure 13).



Figure 13. "Slumping" in 5% Surfactant Parts

Future experimentation will investigate the following issues:

1. determine if we can increase solid loading to higher levels by increasing the mean diameter of the PZT ceramic particles to six microns;
2. determine the highest level of surfactant that does not cause "slumping;" and
3. investigate injection-molding factors.

¹ SAND2005-TBD; The Effects of Process Parameters on the Rheology of Injection-Molded PZT Ceramics-Molding Process

² Applied Fluid Rheology, J. Ferguson & Z. Kemblowski, Elsevier Applied Science, New York, 1991, pp. 52-55.

³ Statistics For Experimenters, G.E.P. Box, W.G. Hunter & J.S. Hunter, John Wiley & Sons, Inc., 1978.

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